Report for 2003WV16B: WRI54: Passive Treatment of Cl Contaminated Waters in NW West Virginia Using Passive Absorptive Technologies

There are no reported publications resulting from this project.

Report Follows

DRAFT

Treatment of Chloride Contaminated Mine Water in NW West Virginia
WVWRI Project wri 54

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Introduction

As underground coal mining recovers coal at greater depths in the Pittsburgh Coal Basin, increasing concentrations of chloride are appearing in the infiltrating water. This, in turn, is typically pumped for discharge and may or may not requirement with hydrated lime to control acid mine drainage parameters such as acidity, iron, aluminum and manganese. In-stream and drinking water limits for chloride are generally 250 mg/L. Chloride is a highly soluble anion and it does not respond to the typical hydroxide precipitation used in the mining industry. However, it is known that both iron and aluminum hydroxide flocs will, under a range of pH conditions develop anion exchange. The objective of this study was to evaluate the potential to remove chloride from solution by using readily available metal flocs produced in treating acid mine drainage. Specifically, we sought to identify the pH range in which anion exchange developed on the metal hydroxide flocs would effectively remove chloride ion, the removal rates of iron vs. aluminum hydroxides and the degree of chloride loading that each of these hydroxide flocs could sustain.

This project investigated the ability of flocculent hydroxide precipitates of aluminum and iron (III) to absorb chloride ions from aqueous solutions developed in the laboratory. Gravimetric analysis was used as the benchmark to monitor the amount of chloride partitioned between the aqueous layer and the precipitate. Both iron and aluminum hydroxide flocs were evaluated: those formed through precipitation prior to and after addition of chloride ion and several sources that were formed in the field as a result of acid mine drainage treatment. The efficacy of ICP as an analytical method to apply to these samples was investigated and compared to the gravimetric results.

Three treatment schemes were tested:

1.   floc precipitation prior to chloride addition
2.   floc precipitation after chloride addition
3.   addition of metal hydroxide flocs collected in the field

Experimental methods are discussed below.

Methods

Sample preparation:

Stock solutions were prepared as follows. The aluminum solution was made by dissolving 100.0 g of $Al_2(SO_4)_3•18H_2O$ in a 1 liter volumetric flask. The iron(III) solution was made by dissolving 100.0 g of $Fe_2(SO_4)_3•9H_2O$ in a 1 liter volumetric flask. The chloride solution was made by dissolving 31.54 g of KCl in a 1 liter volumetric flask. Deionized water was used to make all solutions.

All samples were prepared by pipeting 25 mL of a metal solution and then 25 mL of the chloride solution into a beaker. Precipitation was accomplished by the addition of small quantities of saturated NaOH to bring the pH up into the target range of 4 < pH < 9. The NaOH was added before the chloride in some samples and after the chloride in others. Each sample thus prepared contains 2.5 grams of the hydrated metal sulfate and 0.375 g chloride in a total volume of approximately 50 mL.

After equilibrating, the sample was filtered. The filtrate was sealed in a labeled sample tube and the precipitate was transferred to a beaker. The filter paper was washed with four 25mL portions of 5% nitric acid and the washings are added to the beaker. The precipitate was redissolved by heating on a hot plate adding additional 5% nitric acid if necessary. The solution was filtered again to remove any remaining particulate matter.

Preparation of Controls:

Three DI water samples (18 MOhm/cm) were run through the method to determine effects of contamination and method errors. Zero AgCl recovery was the theoretical result. The actual result was 0.001067g +/- 0.001804g so method errors are minimal on the order of 1mg.

One goal of the initial experiments was to determine if the high throughput ICP at WVSU could be used for experiments of this type. As this was unknown an independent standard like gravimetric analysis was desirable. The ICP consumes the aqueous samples during testing. I wanted to know how reliable it would be to analyze the sludge not sent through the ICP and independently determine the chloride content in the ICP sample by subtraction from the total original chloride present.

Recovery Tests:

A set of eleven samples were selected and the ICP was not used at all. Both the sludge and the aqueous layer were tested for chloride gravimetrically. The theoretical recovery calculated by formulation is 1.5160g AgCl. One experiment showed up as an obvious outlier. After removing this data point the actual recovery was 1.545g +/- 0.033g.

Independent determination of chloride content in samples sent into the ICP should be reliable to within 8mg (33mg AgCl).

Although not set up for this purpose this spreadsheet data shows that a ballpark figure of 35% +/- 5% of aqueous chloride was taken up by the aluminum or iron hydroxide sludges.

Gravimetric analysis:

Samples were diluted to a total volume of 250 mL and mixed with 50 mL of saturated Ag_2SO_4 . The precipitate was digested on a hotplate until the solution was transparent. Additional saturated Ag_2SO_4 was added as a test for completeness. The AgCl precipitate is collected on a weighed filter paper, dried and weighed again.

Three DI water samples (18 MOhm/cm) were run through the method to determine effects of contamination and method errors. Zero AgCl recovery was the theoretical result. The actual result was $0.001067g \pm 0.001804g$ so method errors are minimal on the order of 1mg.

A set of eleven samples was selected and both the precipitate and the aqueous layer were tested for chloride gravimetrically. The theoretical recovery calculated by formulation was 1.5160g AgCl. One experiment showed up as an obvious outlier. After removing this data point the actual total recovery was $1.545g \pm 0.033g$.

In experiments where the aqueous layer was analyzed using the ICP, independent determination of chloride content in the aqueous layer was made by analyzing the precipitate gravimetrically and subtracting the AgCl found from 1.545 g. Samples sent into the ICP had an independent chloride measurement reliable to within 8mg.

ICP analysis:

The model used to analyze the ICP results assumes that chloride is taken up by the metal hydroxide precipitates but potassium is not. Potassium acts as an internal standard. The ratio of the chloride measurement to the potassium measurement in a set of standard KCl solutions provides a reference quotient $Cl_{ref}/K_{ref} = Q_{ref}$. The aqueous phase of a sample yields a sample quotient

$Cl_{samp}/K_{samp} = Q_{samp}$. The percent chloride absorption as a function of the ICP signals is $= 100\% * (1 - Q_{samp}/Q_{ref})$.

Using the ICP is much faster and more convenient than doing gravimetric analysis on the samples but there is currently an unknown systematic error in effect that causes the ICP results to show % chloride absorptions that are on average 11.6% larger that those indicated by gravimetric analysis. When plotted together the results of both methods seem to track each other well except for the offset which seems larger than the estimated error bars would permit. Further refinement of this method is suggested before relying on it as a sole source of chloride concentration measurements

Summary of Results

Chloride absorption was observed for both aluminum and iron hydroxides. 14 aluminum samples showed an average absorption of 35.9% ± 6.6% and 14 iron samples showed an average absorption of 40.5% ± 6.9% . There is an apparent stoichiometry of M_2Cl . There is not enough evidence to support the formation of a compound but it is useful to quantify the observed chloride absorbing capacity. The actual mole ratios observed were Al:Cl = 1.98:1 and Fe:Cl = 2.08:1.

Samples were equilibrated between 50-150 hours. Absorption increased with equilibration time but not significantly enough compared to the experimental uncertainty to obtain reliable kinetic information. The data suggests that the reaction occurs at a rate fast enough that in the first two days these systems absorb roughly 3-4 times as much chloride as they do in the following 4 days.

Adding the chloride to a preexisting precipitate vs. precipitating the metal in the presence of the chloride showed no significant effect compared to experimental error when measurements were taken 50-150 hours after mixing. The precipitation method is suspected to have an impact if measurements are made at shorter times after mixing.

The absorption did not show a strong pH dependence, however at pH values of 4 and lower and 9 and higher the iron or aluminum concentrations in the aqueous phase began to rise above the 1 ppm level. An operating range of 4.5 < pH < 8.5 is recommended to reduce chloride levels without enriching the aqueous phase in metal ions.

Environmental samples of AMD precipitates displayed no activity. The average measured absorption from the aqueous phase of six different samples was -2.7%. However, digested natural precipitates had a chloride content comparable to artificial samples that had absorbed 45.6% of the chloride provided. A hypothesis is that natural AMD precipitates have already saturated

themselves with chloride and only newly precipitated metal hydroxides can display measurable chloride uptake.

ICP analysis of the chloride absorption process yielded results 11.6% higher than the gravimetric control. It is suspected that the chloride response is significantly nonlinear and that narrowing the concentration range of the standards used would be helpful.

Conclusions

Both iron and aluminum hydroxide flocs were effective at scavenging between 35 and 50% of chloride over a pH range of 4 to 9. Iron hydroxide had higher affinities for chloride, accounting for higher removal rates. Iron hydroxide flocs had slightly higher chloride removal rates at higher pH while NaOH addition had no effect either on aluminum hydroxide solution pH nor chloride removal rates. Removal rates were about two moles of either iron or aluminum to each mole of chloride removed. It is noted that the concentrations of both metal ions and chloride used in this laboratory study are about an order of magnitude higher than the highest concentrations normally encountered in mine drainage in West Virginia.

Precipitating the metal flocs prior to or after chloride addition to the solution had no effect on removal rates.

Four mixtures of iron and aluminum hydroxides were collected from an acid mine drainage treatment site in Putnam County, WV. While they removed less than 3% of solution chloride, it was found that they were already saturated with chloride.

The results were surprisingly positive and hold the prospect of a cost effective chloride removal method. It will first be necessary to identify the extent to which metal flocs formed in treating acid mine drainage are saturated with chloride. Those that are not should be evaluated for their potential to remove chloride through simple kinetic/mixing experiments. These will form the basis for designing a full scale field treatment process.
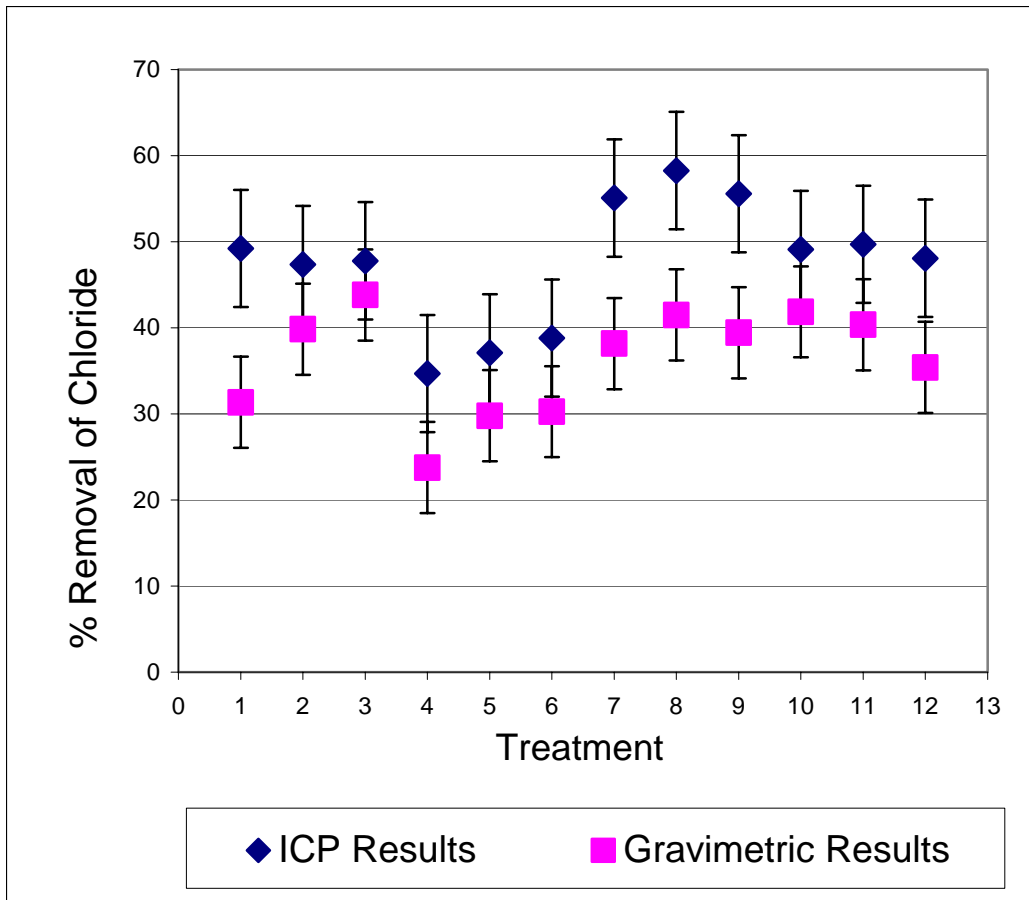
Figure 1.　　Chloride removal was influenced by the nature of the metal flocs while ICP method apparently introduced a positive bias. Each number on the X axis represents an treatment combination as subjected to increasing base additions. Table 1 explains the treatment numbers and solution pHs.

Table 1. Development of the test solutions and resulting ion concentrations.

Source (amount added to 1 L water)	target element	stock solution mg/L	test solution mg/L	mmoles
100g Al$_2$(SO$_4$)$_3$ 18(H$_2$O))	Al	8,108	4,054	150
100g Fe$_2$(SO$_4$)$_3$ 9(H$_2$O)	Fe	19,872	9,936	178
31.54g KCl	K	16,531	8,266	211

Table 2. Proportional chloride removed by twelve experimental combinations. The pH data indicate the realized solution values when the researchers added three increasing amounts of NaOH to each treatment. Note that while base additions increased the pH of the iron flocs they had no effect on the aluminum flocs.

experiment no.	pH	sample ID	treatment description	% Chloride removed ICP	Gravi-metric
1	4.22	fepre1	Iron flocs precipitated prior to Chloride addition	49.2	31.3
2	4.93	fepre5	Iron flocs precipitated prior to Chloride addition	47.4	39.8
3	9.32	fepre6	Iron flocs precipitated prior to Chloride addition	47.8	43.8
4	4.01	alpre4	Aluminum flocs precipitated prior to Chloride addition	34.7	23.8
5	4.01	alpre5	Aluminum flocs precipitated prior to Chloride addition	37.1	29.8
6	4.01	alpre6	Aluminum flocs precipitated prior to Chloride addition	38.8	30.3
7	4.03	feco1	Iron flocs precipitated after Chloride addition	55.1	38.2
8	6.49	feco4	Iron flocs precipitated after Chloride addition	58.3	41.5
9	8.96	feco5	Iron flocs precipitated after Chloride addition	55.6	39.4
10	3.95	alco4	Aluminum flocs precipitated after Chloride addition	49.1	41.9
11	3.93	alco5	Aluminum flocs precipitated after Chloride addition	49.7	40.4
12	3.93	alco6	Aluminum flocs precipitated after Chloride addition	48.1	35.4
		average		47.6	36.3